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FLOCCULATION PHENOMENA IN TURBID WATER CLARIFICATION

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SANITARY DIVISION

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AMERICAN SOCIETY OF CIVIL ENGINEERS

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PAPERS

FLOCCULATION PHENOMENA IN TURBID WATER CLARIFICATION

By W. F. Langelier,[1] Harvey F. Ludwig,[2] Assoc. M. ASCE, and Russell G. Ludwig,[3] Jun. M. ASCE

Synopsis

Inorganic turbidity in natural waters consists principally of clay particles derived from the soil. These particles range up to 5μ in diameter, but the particles smaller than 1μ are the most stable and are of controlling importance in rapid flocculation. These smaller particles are characterized by and derive their stability from an electrical double layer surrounding each particle, the outer layer of which comprises exchangeable cations such as Na^+, K^+, Ca^{++}, Mg^{++}, and H^+. The addition of polyvalent cations such as Al^{+++}, Fe^{+++}, or other coagulants to the water will repress the double layer and lower the stability of the particles. At a critical level of destabilization, the particles begin to coalesce, forming aggregates, at a rate dependent upon the exchange capacity of the particles. In most natural waters this rate of aggregation is slow, and some mechanical binding agent, such as hydrous aluminum oxide, is also required to accelerate aggregation and effect rapid clarification. In practice, a properly adjusted dosage of a single hydrolyzing coagulant chemical, such as alum, will effect both the destabilizing and the mechanical binding actions.

Optimum flocculation represents the attainment of a complex equilibrium in which many variables are involved, including turbidity, particle size distribution, exchange capacity, pH, and alkalinity. Alkalinities above and below optimum result in excessive and insufficient production of binder material, respectively. Smaller clay colloids of less than 1μ size are necessary for stabilizing the hydrous oxide particles through mutual coagulation, and for

inducing agglomeration of other large particles present.   Larger particles of 1 to 5μ size are needed to serve as building units, to form compact and dense flocs.   If the water is initially deficient in colloids, its flocculation behavior may be improved by the addition of bentonites, activated silica, or other negatively charged colloidal material.

INTRODUCTION

Flocculation, as employed in the clarification of turbid water, has been the subject of many excellent papers extending over many years.   Some of the most widely quoted of these[4,5,6,7,8] have dealt principally with the behavior of various coagulants as affected by the chemical properties of the water, but without particular consideration of the character of the dispersed phase.   The authors have previously described results of flocculation experiments conducted with dilute suspensions prepared from known types of clays.[9]   This paper briefly reviews the conclusions drawn therefrom and includes additional data amplifying the concepts previously developed.

In the earlier paper it was concluded that rapid flocculation of turbid water with alum normally comprises two distinct reactions, one involving partial destabilization of turbidity particles by aluminum ions through ion exchange, the other involving formation of a hydrous oxide gel, resulting from hydrolysis of the coagulant that serves as an agglomerating agent or binder material. In the treatment of most waters, a properly adjusted dosage of a hydrolyzing coagulant, such as an aluminum or ferric salt, will satisfy both demands economically, but in some cases a preadjustment of buffer capacity and pH may improve performance and reduce cost by the alteration of the relative proportions of coagulant entering into the two basic reactions.   In this concept, the phenomenon of mutual coagulation, which assumes the formation of positively charged hydrous oxide particles, is believed to be of secondary importance. Mutual coagulation may assist in bringing about destabilization of turbidity particles and may aid the agglomerating action by facilitating the rapid agglomeration of newly forming hydrous oxide particles, but mutual coagulation is not essential to either process.   Support of this belief is furnished by data showing that as the exchange capacity of the suspension increases above a critical limit, rapid flocculation and clarification is effected through the use of chemicals that do not hydrolyze to form insoluble hydroxides.

[4] "Coagulation of Water with Alum by Prolonged Agitation," by W. F. Langelier, *Engineering News-Record*, Vol. 86, 1921, p. 924.

[5] "An Experimental Study of the Relation of Hydrogen Ion Concentrations to the Formation of Floc in Alum Solutions," by Emery J. Theriault and W. Mansfield Clark, *Public Health Reports*, U. S. Public Health Service, Washington, D. C., Vol. 38, 1923, p. 181.

[6] "Alumina Floc—X-Ray Diffraction Study," by Henry B. Weiser, W. O. Milligan, and W. R. Purcell, *Industrial and Engineering Chemistry*, Vol. 32, 1940, p. 1487.

[7] "Effect of Salts on the Rate of Coagulation and the Optimum Precipitation of Alum Floc," by Ben H. Peterson and Edward Bartow, *Industrial and Engineering Chemistry*, Vol. 20, 1928, p. 51.

[8] "Formation of Floc by Aluminum Sulfate," by Edward Bartow, A. P. Black, and Owen Rice, *Industrial and Engineering Chemistry*, Vol. 25, 1933, p. 811.

[9] "Mechanism of Flocculation in the Clarification of Turbid Waters," by W. F. Langelier and H. F. Ludwig, *Journal*, American Water Works Association, Vol. 41, 1949, p. 163.

Two equivalent representations of this concept of flocculation are shown in Fig. 1. For an ordinary water, the turbidity of which exhibits a relatively low exchange capacity, there are two possible flocculation zones: (1) Primary or normal flocculation; and (2) secondary or high-range flocculation. In normal flocculation the added coagulant is involved simultaneously in both an exchange and a hydrolysis reaction. In secondary flocculation, that is, in the presence of an excess of coagulant, destabilization and flocculation are brought about solely by the high concentration of active cations (Al^{+++} and H^+ ions). Fig. 1 shows that as exchange capacity of the turbidity progressively increases, the zone of normal flocculation moves to the right and becomes increasingly wider. At the same time the onset of secondary flocculation occurs in the presence of correspondingly less coagulant. At and above a certain critical exchange capacity the two flocculation zones merge. At still higher exchange capacities,

(a) GRAPHICAL REPRESENTATION OF FLOCCULATION PHENOMENA AS RELATED TO EXCHANGE CAPACITY
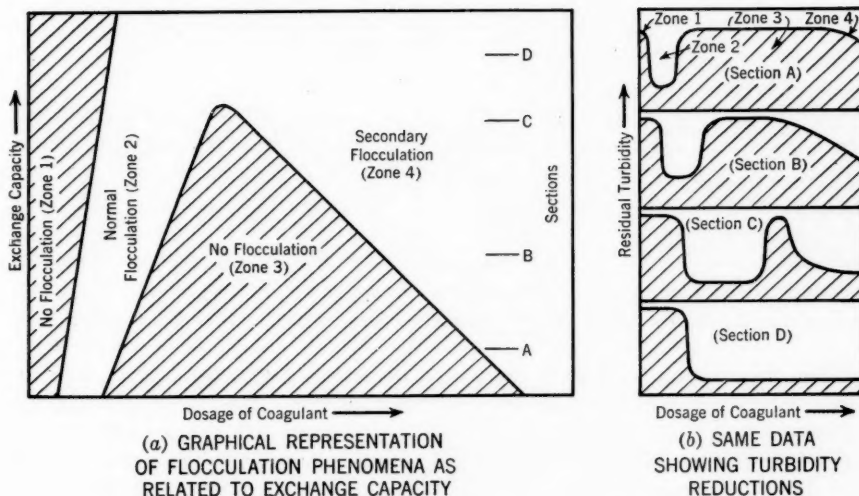
(b) SAME DATA SHOWING TURBIDITY REDUCTIONS

FIG. 1.—FLOCCULATION PHENOMENON RELATED TO EXCHANGE CAPACITY AND TURBIDITY REDUCTION

secondary flocculation supercedes the primary type, and excellent flocculation and clarification occur in the absence of hydrolysis. The exchange capacity of a given water can be increased by the addition of negatively charged colloids, as, for example, activated silica, bentonite, and various other materials. For waters of less than optimum turbidity or exchange capacity, the addition of such substances may greatly improve flocculation and clarification within the primary or normal range. The added particles, through their capacity to agglomerate rapidly when destabilized, promote the agglomeration of all of the suspended particles present. Also, the added particles may furnish buffer capacity that is valuable in the event the chemical alkalinity of the system is low. In addition, as will be discussed later, these negatively charged colloids may be helpful in improving the density of the flocs.

EXPERIMENTAL PROCEDURE

In Table 1 are given the properties of synthetic turbid waters prepared from six different representative types of soils. These suspensions were made by dispersing the original soil mass in distilled water and then allowing the suspension to settle for 24 hr, after which a proper depth of supernatant was siphoned off to include only particles of approximately 1.40μ ($1\mu = 0.001$ mm) diameter or less. The resulting turbidities ranged from 45 to 63 ppm. In this approximate range of turbidity the separate effects of the different flocculation variables are accentuated. In Table 1 the initial buffer capacity is the acid titre of the suspension, and is the result of exchange adsorption of hydrogen ions by the clay particles. Exchange capacity is a property of the suspension obtained by multiplying the weight of the suspended particles (obtained by evaporation) by their exchange or saturation capacities as measured by the standard acetate procedure employed in soil technology.

TABLE 1.—PROPERTIES OF SYNTHETIC TURBID WATERS

Soil type employed	Initial turbidity (ppm)	pH	Initial buffer capacity (ppm) as $CaCO_3$	Approximate exchange capacity (milliequivalents per liter)
Yolo silty clay loam...............	60	7.0	4	80
Aiken clay loam....................	62	7.0	4	15
Dublin clay.......................	60	6.9	3	100
Fresno sandy loam.................	45	7.3	5	50
Panoche fine sandy loam...........	62	7.3	4	20
Holland sandy loam................	58	7.0	4	10
Average...........................	58	7.1	4	45

The flocculation tests were conducted in batteries of 200-ml jars, each jar being equipped with a slowly revolving paddle. Ten min of stirring followed by 15 min of quiescence were allowed, after which the top 100 ml was poured off and reserved for turbidity and pH measurement. The test data also included several other criteria, such as floc quality, time of floc formation, rate of floc settling, and size and quality of floc. Almost invariably, however, it was found that the turbidity reduction alone constituted an adequate criterion of optimum flocculation, for, in order to secure a low residual turbidity, each of the other factors had also to be at or near its respective optimum condition.

Five series of flocculation tests, employing alum as a coagulant, were undertaken for each of the six synthetic waters. In addition, two series of tests were made to study other pertinent factors. The test series are listed in the following tabulation:

Test series   Description

I. Varying concentrations of $NaHCO_3$, to indicate effects of bicarbonate alkalinity.

II. Varying concentrations of either NaOH or $Ca(OH)_2$, for adjustment of pH and buffer capacity.

III. Varying concentrations of either NaCl or Na_2SO_4, for anion or salinity effects.

| Test series | Description |

IV. Varying concentrations of sodium hexametaphosphate and sodium versenate, as examples of sequestering or chelating agents.

V. Varying concentrations of various surface active agents.

VI. Tests to determine the relative behavior of various hydrolyzing coagulants, such as aluminum sulfate, aluminum chloride, ferric chloride, ferric sulfate, thorium nitrate, and lanthanum chloride.

VII. Tests to study turbidity particle size distribution as related to coagulant demand.

In all tests following Series I the samples were buffered with 0.5 milliequivalents per liter of $NaHCO_3$. This concentration of buffer or alkalinity was found to be the optimum, for the range of turbidities studied, for distinguishing the separate effects of the other variables.

INTERPRETATION OF EXPERIMENTAL DATA

Effect of Bicarbonate Alkalinity.—The pertinent results of the Series I tests, which were made with $NaHCO_3$ added as buffer in amounts of 0, 0.20, 0.50, and 1.00 milliequivalents per liter, are illustrated in Fig. 2. For each water the plotted points represent the most efficient dosages (D_e) for the various total alkalinities (B). This total alkalinity includes the titratable alkalinity of the turbidity particles. Also, at each plotted point is shown the final pH-value (pH_e) corresponding to the most efficient dosage. These curves are seen to be a series of straight lines, showing: (*a*) That different soil suspensions exhibit different coagulant demands; (*b*) that an increase in buffer capacity results in a proportionate increase in coagulant demand; and (*c*) that within the limits of the tests pH_e increases with total alkalinity.
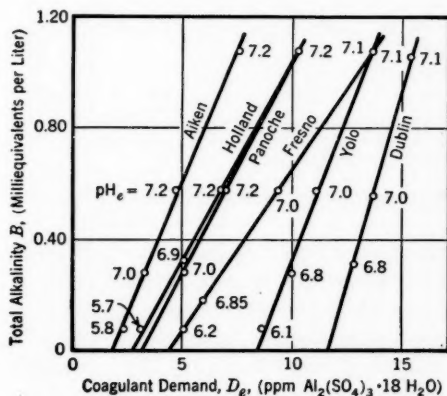
FIG. 2—COAGULANT DEMAND OF SOIL SUSPENSIONS IN WATERS OF VARYING TOTAL ALKALINITY
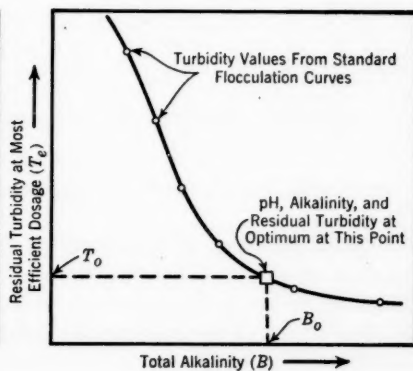
FIG. 3.—OPTIMUM FLOCCULATION CONDITIONS FOR A GIVEN WATER

If, for a given suspension, the various values of total alkalinity are plotted against the corresponding residual turbidities (T_e) at most efficient dosage, a curve of the type shown by Fig. 3 is obtained. Examination of this curve permits selection of the minimum value of total alkalinity at which good

clarification occurs, and beyond which the resulting improvement in clarification is small compared with the increase in coagulant that will be required to obtain this clarification. This alkalinity may properly be termed the optimum alkalinity (B_o), because it represents the greatest turbidity reduction obtainable commensurate with an economical coagulant dosage. The pH_e value associated with this optimum value may be termed the optimum pH for that water, pH_o, and the most efficient dosage at that alkalinity the optimum dosage (D_o). For the six suspensions studied, the optimum alkalinity was from 0.5 to 0.8 milliequivalents per liter in every case, and the corresponding optimum pH values varied between the narrow limits of 7.0 to 7.2.
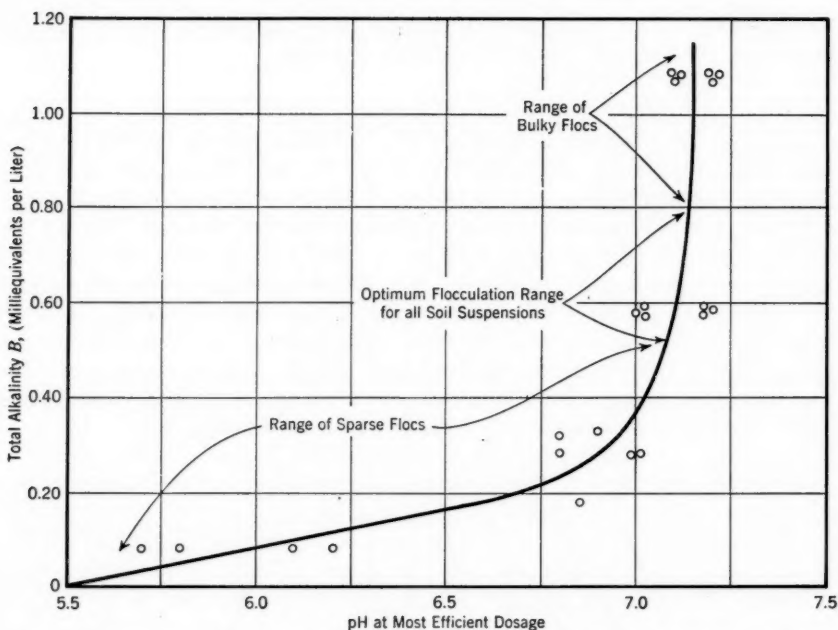

FIG. 4.—RELATIONSHIP BETWEEN TOTAL ALKALINITY AND pH AT MOST EFFICIENT ALUM DOSAGE

Fig. 4 has been plotted to show a typical variation in values of pH_e with increasing bicarbonate alkalinity. From this curve it is interesting to note that the value of pH_e increases with total alkalinity until reaching a maximum of about 7.1. This relationship indicates that alkalinity in excess of optimum results in the waste of an equivalent amount of coagulant. In the treatment of waters of this type it may be advantageous to neutralize a portion of the alkalinity with a strong acid prior to the addition of coagulant.[4] A probable explanation of this phenomenon may lie in the fact that in the presence of hydroxyl ions the added aluminum ions form soluble complexes. Thus, when the initial pH is greater than optimum, the alum first added to the water would not form hydrous oxide but instead would combine with OH^- ions to form complex aluminate anions, liberating hydrogen ions. The continued removal of

OH^- will eventually lower the pH to the optimum, at which point further addition of alum effects the normal reactions. Since at this point most of the complex cations would be converted to hydrous oxide, the resulting floc is bulky.

Referring again to Fig. 2, it will be noted that, although all of the suspensions have about the same initial turbidity and alkalinity and have approximately the same pH_o and B_o values, they exhibit variable coagulant demands. At constant alkalinity of 0.5 milliequivalents per liter the coagulant demands vary from about 4.5 ppm to 13.5 ppm. A comparison of the D_e values with the exchange capacities for the various suspensions shows that, in general,
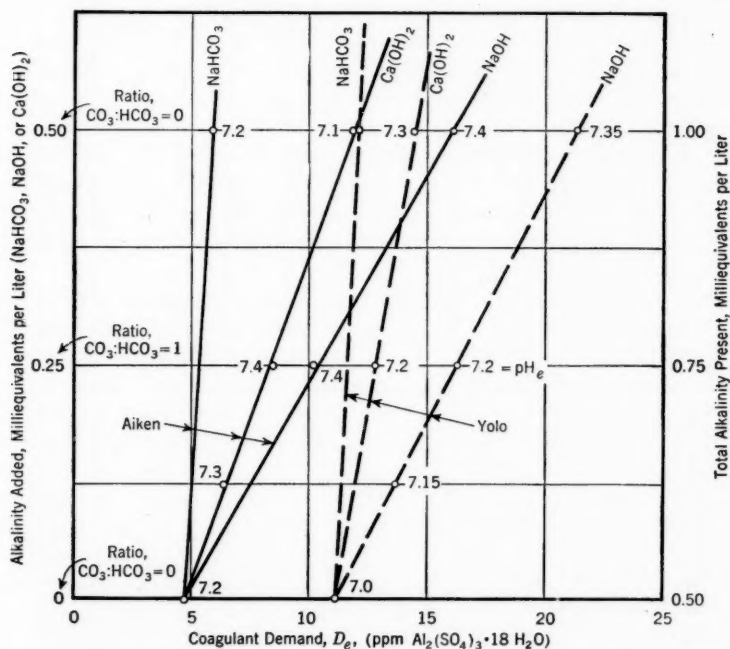
Fig. 5.—Effect of CO_2 — HCO_3 Ratio on Alum Demand at Constant Total Alkalinity

values of D_e increase in an amount equal to the exchange capacity, indicating that greater amounts of Al^{+++} ions are needed for destabilizing the particles of greater exchange capacity. The lack of an absolutely consistent relationship between the values for D_e and the exchange capacity is probably in part the result of the variation in size distribution of the turbidity particles. The Series VII studies, discussed subsequently, were undertaken to investigate this factor.

Adjustment of pH and Buffer Capacity.—The Series II tests were made to determine the effect on alum coagulant demand of variable ratios of carbonate and bicarbonate alkalinity. For this purpose, varying increments of either sodium or calcium hydroxide were added to the bicarbonate suspensions.

The results for suspensions of two clay types that are typical are shown in Fig. 5.   The curves in this figure indicate that the coagulant demand for a given total alkalinity increases as the ratio of carbonate to bicarbonate increases. The reason for this is apparent, when it is noted that efficient coagulation under the conditions of the test procedure occurs only upon the addition of sufficient alum to lower the pH to an approximately constant value of from 7.1 to 7.2.   The amount of alum (or acid) required for this purpose is a function of both total alkalinity and buffer capacity, that is, the amount depends upon the types of alkalinity present and the buffer properties of these types in the pH range considered.   The separate effects of total alkalinity and of buffer capacity in the region above pH 7.2 are indicated by the relative slopes of the curves marked $NaHCO_3$ and NaOH.   The fact that the $Ca(OH)_2$ curves fall to the left of the NaOH curves is attributed partly to the destabilizing effect of the divalent calcium ions upon the turbidity particles and partly to the possible formation of colloidal calcium carbonate.

The effects noted would not necessarily hold in normal waters containing calcium ions because of secondary reactions involving the precipitation of colloidal calcium carbonate.   In waters of low turbidity or alkalinity, pretreatment with lime may serve a useful or even essential purpose in effecting a better balance between the two basic equilibria involved in normal flocculation.

Anion or Salinity Effect.—The Series III tests were conducted to determine to what extent certain salts of strong acids and bases might influence flocculation behavior.   To the six turbid waters, varying amounts of NaCl (and, in another test group, Na_2SO_4) were added, and for each water the values of D_e and pH_e were determined. Typical results are shown in Fig. 6.   Two effects are noted as due to the presence of NaCl or Na_2SO_4 in appreciable concentration:
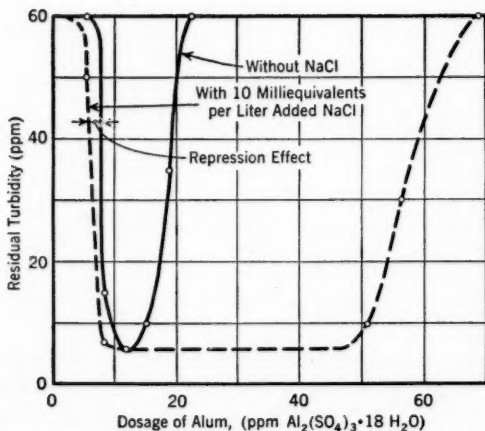
FIG. 6.—EFFECT OF SODIUM CHLORIDE ON ALUM DEMAND AND RESIDUAL TURBIDITY

1. The Na^+ ions exert a slight destabilizing effect, as illustrated by the slight decrease in coagulant demand. This phenomenon is in agreement with colloid theory, and may be attributed to a repression rather than an exchange effect caused by the high concentration of cations in the water medium surrounding the negatively charged suspended clay particles.

2. The zone or range of effective clarification is appreciably widened. This effect is similar to that obtained by increasing the buffer capacity of the

system, but must be due to a different cause. The phenomenon has been noted and discussed by B. H. Peterson and Edward Bartow,[7] M. ASCE, and by Mr. Bartow, A. P. Black, and Owen Rice.[8]

Another observation made in this series of tests was that large dosages of either NaCl or Na_2SO_4, beginning at roughly 400 ppm, had a detrimental or dispersing effect on floc formation, resulting in a fine, slow-settling floc. Similar results have been observed in attempts to flocculate turbid sea water. H. T. S. Britton[10] notes that the chloride ion has a dispersing action on hydrous oxide micelles, and through peptization tends to prevent their formation. In the studies mentioned in this paper, however, similar phenomena occurred in the presence of either chloride or sulfate. A more likely explanation is that suggested by the work of Henry Bassett and Reginald Durrant.[11]

In discussing their "emulsoid" theory of hydrous oxides, these researchers report that the hydrous oxide micelle is essentially a very viscous or glassy liquid, with or without a crystalline core, that is separated from the surrounding water medium by an electric double layer made up of fixed cations and of oscillating counter anions. In addition, some of the fixed cations, and with them their accompanying anions, may infiltrate or pass through the particle surface into the viscous medium and so modify its composition from an initial essentially hydrous aluminum oxide to a combination of this oxide with aluminum chloride or sulfate. The degree to which such infiltration occurs is a mass action phenomenon, so that when a large amount of a salt such as NaCl or Na_2SO_4 is added to the system many of the resulting cations and anions pass into the micelle, until eventually it no longer exists as a separate mass of hydrous oxide but passes into solution.

Effect of Sequestering or Chelating Agents.—In the Series IV tests, sodium metaphosphate and sodium versenate (a sodium salt of ethylene digmine tetracedic acid) were employed as representative sequestering or chelating substances that in practice have been noted to interfere with normal flocculation behavior. The data from tests made with Yolo suspensions of 0.5 milli-equivalents per liter alkalinity and 60 ppm initial turbidity are illustrated in Fig. 7. The alum dosage (D_e) increases linearly as the concentration of meta-phosphate or of versenate is increased. For metaphosphate the relationship is approximately as follows:

$$D_e = 4.86\,C + 11.2 \dots\dots\dots\dots\dots\dots\dots (1)$$

in which C is the concentration of sodium metaphosphate in ppm and D_e is in ppm of $Al_2(SO_4)_3 \cdot 18\,H_2O$. Thus, at an alkalinity of about 0.5 milli-equivalents per liter, the presence of a unit weight of metaphosphate requires an increase in alum dosage of almost five units, if the flocculation results are to be satisfactory. It is significant, however, that the quality of the flocs produced at most efficient dosage progressively decreases as the concentration of meta-phosphate increases. Furthermore, at metaphosphate concentrations of 5 ppm or more, normal alum flocculation could not be obtained regardless of the amount of alum added.

[10] "Hydrogen Ions," by H. T. S. Britton, Chapman & Hall, Ltd., London, 1932.

[11] "Equilibria and Changes in Metal Hydroxide Sols," by Henry Bassett and Reginald G. Durrant, *Journal*, The Chemical Society, London, 1942, p. 277.

The specific manner in which the metaphosphate causes this effect cannot be positively ascertained with the data at hand.   The metaphosphate, through its sequestering properties, could conceivably interfere with both the destabilizing phase and the binder-agglomeration phase of the flocculation process. Mr. Bassett and Mr. Durrant[11] note that metaphosphates may partially prevent the hydrolysis of aluminum and ferric salts, and also that the hydrous oxide that does form will be peptized or dispersed.   The observed data are readily explained by application of this information; thus, metaphosphate inhibits the formation of proper binder, sequesters the polyvalent cations, and probably
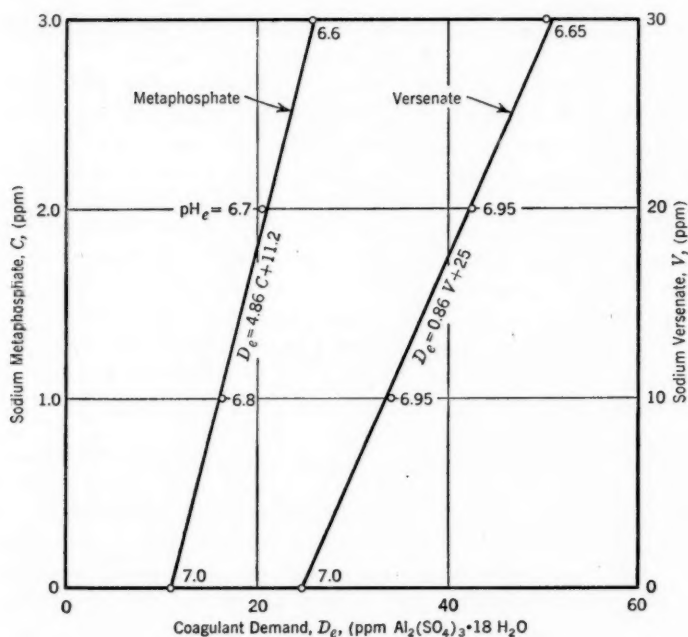
Fig. 7.—Effect of Sequestering Agents on Alum Flocculation

also tends to peptize the clay turbidity particles and increase their resistance to destabilization.   At low concentrations of metaphosphate the first two of these adverse effects may be overcome simply by increasing the coagulant dosage to provide the necessary excess alum over that amount inactivated by the metaphosphate; but even so the peptization of the clay particles results in an inferior floc.   At high concentrations of metaphosphate the peptization of the clay particles may be so complete that no dosage of alum can affect their agglomeration.

It is interesting to note that the effect of metaphosphate on flocculation can scarcely be attributed to formation of complex sodium-aluminum-phosphate anions in stoichiometric proportions.[12]   For stoichiometric sequestration, the

[12] "Sequestration, Dispersion, and Dilatancy—Lecture Demonstrations," by T. H. Daugherty, *Journal of Chemical Education*, Vol. 25, 1948, p. 482.

amount of metaphosphate needed to sequester 1 milliequivalent per liter of Al^{+++} would be of magnitude of 100 to 200 ppm, whereas only 22.8 ppm are actually required. A possible explanation is that the metaphosphate consists of chains of molecules, the chains being of various lengths and intertwined so that the amount of aluminum ions sequestered by the metaphosphate molecule $(NaPO_3)_n$ could be much greater than indicated by the stoichiometric relationships. Another possible explanation assumes the formation of Werner complexes, in which a metaphosphate anion replaces one or more of the aqua groups attached to the hydrated Al^{+++} ion.

The results obtained with sodium versenate were similar to those obtained with metaphosphate, except that more versenate than metaphosphate is required to produce the same results. Also, it was possible to effect flocculation in the presence of as much as 170 ppm versenate, simply by adding sufficient alum; and the linear relationship extended over the entire 0 to 170 ppm range.

Effect of Surface Active Agents.—The Series V tests involved the effects of a number of the synthetic surface active agents on the flocculation of Yolo type suspensions. In recent years these agents have come into wide use both in the home and in industry. One of the common properties of these substances is their ability to disperse colloidal particles, and in this action they achieve the opposite of flocculation or deflocculation. The various agents investigated included representatives of the anionic, cationic, and nonionic groups. As was anticipated, the results obtained varied widely for different agents. Of the anionics, Santamerse Number 1, an alkylarylsulfonate that is typical of the type of synthetic surface active agent now being produced in greatest quantities, was added in concentrations up to 50 ppm, and had no effect whatever on the flocculation phenomena. Similarly Sterox SE, a nonionic polyoxyethylene thioester, in concentrations up to 0.06% by volume had no noticeable effect. However, Sterox CD, another nonionic, in a concentration by volume of 0.004%, caused complete dispersion of a system that otherwise would have produced an excellent floc. Triton NE, a liquid nonionic polyoxyethylene ester, when added in concentrations by volume up to 2.0%, had only a slight effect on flocculation phenomena, in that it caused a slight increase in residual turbidity obtained with the same dosage of coagulant. Another anionic agent, TDA, interfered very much with normal flocculation behavior. A concentration of 0.005% by volume increased the coagulant demand of the test suspension from 25 ppm alum to 50 ppm, and a concentration of 0.01% by volume increased the coagulant demand to 100 ppm. In both instances the residual turbidity at most efficient dosage increased considerably. Kreelon 4G, an anionic alkylarylsulfonate, showed no effect on flocculation behavior in concentrations up to 17 ppm but at this and higher concentrations effected increasing floc dispersion, reaching complete dispersion at 40 ppm. However, by increasing the alum dosage from its initial value of 25 ppm to 30 ppm the dispersive action was completely overcome, and in fact the resulting flocs were of greatly increased size and density.

Tests were also made with one cationic agent, Hyamine 1622-CRYS, a quaternary compound. Additions of this compound up to 15 ppm did not influence the flocculation behavior, but a dosage of 20 ppm effected complete

dispersion of a system that otherwise would have developed a good floc. Also, increasing the alum doage from its initial demand value of 25 ppm to dosages as high as 100 ppm did not overcome the dispersion effect. The dispersion effect of cationics might be expected to interfere in sewage treatment processes involving flocculation, except that the cationics are not compatible with the anionics, which are manufactured and employed in far greater amounts.

TABLE 2.—FLOCCULATION DATA EMPLOYING

Coagulant	Chemical formula	Yolo			Aiken			Dublin		
		Dosage in milli-equiva-lents per liter	In terms of alum[a]	pH_e	Dosage in milli-equiva-lents per liter	In terms of alum[a]	pH_e	Dosage in milli-equiva-lents per liter	In terms of alum[a]	pH_e
Alum	$Al_2(SO_4)_3 \cdot 18\ H_2O$	0.100	1.00	7.0	0.043	1.00	7.2	0.123	1.00	7.0
Aluminum chloride	$AlCl_3 \cdot 6\ H_2O$	0.100	1.00	7.0	0.046	1.07	7.2	0.131	1.07	6.9
Ferric chloride	$FeCl_3 \cdot 6\ H_2O$	0.230	2.30	6.7	0.150	3.48	6.8	0.220	1.79	6.6
Ferric sulfate	$Fe_2(SO_4)_3 \cdot 9\ H_2O$	0.290	2.90	6.5	0.150	3.48	6.8	0.260	2.11	6.6
Lanthanum chloride	$LaCl_3 \cdot 7\ H_2O$	0.100	1.00	7.2	0.100	2.32	7.15	0.200	1.63	6.9
Thorium nitrate	$Th(NO_3)_4 \cdot 4\ H_2O$	0.300	3.00	6.6	0.150	3.48	6.8	0.200	1.63	6.7

SYNTHETIC

[a] Weight of coagulant required as compared with alum.

Relative Behavior of Various Hydrolyzing Coagulants.—The Series VI tests were made to compare in detail the relative flocculating efficiencies of various salts that hydrolyze to form an insoluble hydrous oxide binder material. For each of the salts or coagulants employed, the most efficient dosage, D_e was determined for each of the six waters, buffered with 0.5 milliequivalents per liter $NaHCO_3$. The required coagulant dosages in milliequivalents per liter are given in Table 2.

The conclusions drawn from these data are as follows:

a. Aluminum chloride dosages are about 15% greater than those required with alum, but otherwise the phenomena are similar. The difference is attributed to the composition of the hydrous oxide micelles as affected by Cl^- and SO_4^- ions. H. T. S. Britton[10] notes that the formation of visible hydrous oxide micelles from a solution of any hydrolyzing salt, when alkali is progressively added, is preceded by a period of formation of colloidal or "soluble" particles too small to be seen or to be effective. The presence of Cl^- ion, either from the use of aluminum chloride or from the water medium, has a dispersing effect that promotes and prolongs the formation of inactive hydrous oxide and so decreases the efficiency of the coagulent. This effect has been described by Lewis B. Miller.[13]

b. Under the conditions of the tests, ferric chloride was more efficient than ferric sulfate, but both were much less efficient than alum on an equivalent basis.

[13] "A Study of the Effects of Anions Upon the Properties of 'Alum Floc,'" by Lewis B. Miller, *Public Health Reports*, U. S. Public Health Service, Washington, D. C., Vol. 40, 1925, p. 351.

c. Inasmuch as Fe^{+++} and Al^{+++} ions are regarded by colloid chemists as being approximately equal in their effect in the destabilization of clays,[14] it is concluded that hydrous ferric oxide binder is much less efficient than hydrous aluminum oxide binder, with approximately three times as much being required. Correspondingly, the pH_e varies obtained with the iron salts are lower than those obtained with the aluminum salts, by about 0.35 pH units.   However,

VARIOUS HYDROLYZING ELECTROLYTES

TURBID WATER DESIGNATION

Fresno			Panoche			Holland			Average		
Dosage in milli-equiva-lents per liter	In terms of alum[a]	pH_e	Dosage in milli-equiva-lents per liter	In terms of alum[a]	pH_e	Dosage in milli-equiva-lents per liter	In terms of alum[a]	pH_e	Dosage in milli-equiva-lents per liter	In terms of alum[a]	pH_e
0.085	1.00	7.0	0.062	1.00	7.2	0.062	1.00	7.2	...	1.00	7.10
0.110	1.29	7.0	0.077	1.24	7.1	0.077	1.24	7.0	...	1.15	7.03
0.190	2.23	6.8	0.140	2.26	6.8	0.140	2.26	6.7	...	2.39	6.72
0.220	2.59	6.7	0.140	2.26	6.8	0.140	2.26	6.7	...	2.60	6.68
0.100	1.18	7.2	0.100	1.61	7.2	0.075	1.21	7.1	...	1.49	7.12
0.250	2.94	6.7	0.150	2.42	6.9	0.200	3.23	6.7	...	2.78	6.73

it should be noted again that the tests were conducted under conditions favorable for alum flocculation; and for waters of different character, the efficiency of the iron salts might compare more favorably.

d. With lanthanum chloride as coagulant the residual turbidities obtained at most efficient dosages are considerably higher than with iron and aluminum salts.   The flocs produced were small and of poor quality.   The La^{+++} ions are undoubtedly effective for destabilization, but apparently not enough binder material of good quality can form to be really effective.   The poor performance of lanthanum may be attributed to the greater solubility of lanthanum hydrous oxide at ordinary pH values.   As shown by Mr. Britton, appreciable quantities of lanthanum hydrous oxide form only at a pH of 8.4 or greater.

e. Thorium nitrate is an effective and very rapid flocculating agent.   In all tests it yielded extraordinarily large flocs.   The turbidity reductions effected at most efficient dosage were considerably better than with any other coagulant.   These excellent results may be attributed to a combination of a very powerful destabilizing agent, Th^{++++}, together with an excellent hydrous oxide binder.   Mr. Britton notes that visible thorium hydrous oxide particles begin to form at pH values as low as 3.5.

f. Considering each of the six salts tested, the pH_e values are lower, as would be expected, in proportion to increased requirements for binder demand. However, the turbidity reductions effected at most efficient dosage are somewhat greater in proportion to this increase in binder demand.   Thus, to produce an effective hydrous iron oxide binder requires three times more ferric than

[14] "Properties of Colloids," by Hans Jenny, Stanford University, Stanford, Calif., 1938.

aluminum salt, but the clarification effected by the iron salts is consistently better to a small but noticeable degree. Similarly, to produce an affective hydrous thorium oxide binder requires about 3.7 times as much thorium salt as alum, but the resulting clarification is even better than that produced by the iron salts.

Effect of Particle Size.—An important variable in coagulant demand is the fineness of the particles that comprise the turbidity. In order to investigate

Fig. 8.—Effect of Particle Size Distribution on Turbidity and Coagulant Demand

the effect of varying particle size distribution, a stock suspension was prepared by dispersing Yolo silty clay loam in distilled water to a concentration of 1,000 ppm. This water had an initial turbidity of 610 ppm. Alum flocculation tests were made to determine its coagulant demand and also the coagulant demand of various dilutions of the stock suspension down to 10%, or 61 ppm, in each case in the presence of 0.5 milliequivalents per liter of $NaHCO_3$.

Other batches of the stock suspension were prepared and allowed to remain quiescent for varying periods of time, ranging from 15 min to 25 hr. Following the designated periods of settling, the top or supernatant 20 cm of each suspension was drawn off, and its coagulant demand similarly determined. In addition, coagulant demand tests were made of each of the settled waters after dilution to obtain uniform turbidities of 100 ppm. The results of these tests are plotted in Figs. 8 and 9.

The upper curve (ABC) of Fig. 8, with scales read from the top, shows the change in coagulant demand for varying turbidities obtained by plain settling and decantation. In the range AB there is practically no decrease in coagulant demand, indicating that particles greater than about 5μ diameter exert little, if any effect. It was noted in making the tests in this range that some of the particles were not incorporated into the flocs but settled rapidly to the bottom of the test jar. In the range BC no separation of particles was noted, but the coagulant demand decreased from 27 ppm to 21 ppm as a result of the absence of particles of diameters from about 5μ down to about 1.5μ. The coagulant demand at point C may be considered as comprising an exchange demand plus a binder demand. Soil technologists have shown that practically all of the exchange capacity of a clay suspension is associated with particles smaller than 1.5μ diameter. Therefore, the exchange demand may

FIG. 9.—EFFECT OF PARTICLE SIZE ON COAGULANT DEMAND WITH A CONSTANT TURBIDITY OF 100 ppm USING YOLO SUSPENSION

be considered practically constant between points B and C, and the decrease in coagulant demand with decreasing turbidity must be the result of a lower binder demand This would be expected since the particles of 1.5–5μ size are incorporated into the floc.

The lower curve (AD) of Fig. 8 shows that the coagulant demand of the diluted stock suspensions, wherein particle size distribution remains unaltered, decreases in almost direct proportion to the decrease in turbidity. The intermediate curves have similar significance. These straight-line relationships indicate that dilution decreases both the exchange and binder demands in equal proportion.

The plotted points on a vertical line of Fig. 8 representing a constant turbidity of 100 ppm, show the variation in coagulant demand caused by differences in particle size distribution. In Fig. 9 these data have been replotted to show maximum particle size diameters. It will be noted that the coagulant
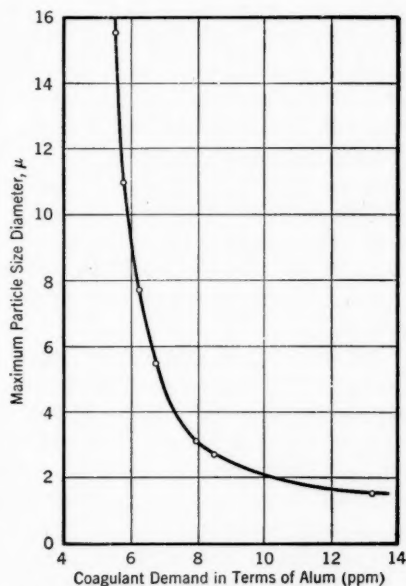
demand increases progressively as the percentage of smaller particles becomes greater, and that the rate of increase is very great when the particles present are predominantly of diameter less than 2μ.

To gain additional information concerning the relationship between coagulant demand and particle size distribution, and also to confirm the results described, a suspension of the Yolo silty clay loam was fractionated by means of repeated subsidence and decantation. On the basis of Stoke's law computations, the suspension was separated into groups containing only particles of the following diameters: 0 to 1μ; 1μ to 2μ; 2μ to 5μ; 5μ to 15μ; 15μ to 25μ; 25μ to 60μ; and those greater than 60μ. The coagulant demand of each of these suspensions was determined. Good flocs, although gelatinous and slow settling, were obtained with the 0 to 1μ fraction, regardless of the value of the turbidity, over a wide range. Surprisingly, none of the other fractions yielded good flocs. A very few sparse flocs were obtained with the 1μ to 2μ fraction, but none at all with the coarser fractions. It was noted, however, that when mixtures of the finest fraction and various coarser fractions were flocculated, all of the particles present were readily incorporated into flocs. Good flocs were obtained in a 1 to 1 mixture of the 0 to 1μ and the 1μ to 2μ fractions of equal initial turbidity. Similar results were obtained in a 2 to 1 to 1 mixture of 0 to 1μ, 1μ to 2μ, and 2μ to 5μ fractions of equal initial turbidity.

An interesting observation resulted from alum flocculation of a 0 to 1μ system of 100 ppm turbidity, to which had been added 25% by volume of a 15μ to 25μ suspension of equal turbidity, as compared with adding 25% by volume of distilled water. In the latter case the coagulant demand was 25 ppm and the corresponding residual turbidity 35 ppm, and the flocs were noted to be gelatinous and slow settling. In the former case the coagulant demand was also 25 ppm, but the residual turbidity was reduced to 10 ppm and the flocs were larger and settled rapidly.

These various observations indicate the role of particle size in alum flocculation. Effective alum flocculation of a turbid water requires, in addition to suitable pH and alkalinity, turbidity particles both finer and coarser than approximately 1μ diameter. The smaller particles possess colloidal properties, and some of these are needed for neutralizing positive charges formed on the hydrous oxide binder particles (mutual coagulation). The aggregation of the colloidal turbidity particles, which results when they are destabilized by a suitable polyvalent cation, appears to induce agglomeration of the larger non-colloidal particles. This agglomerating action facilitates subsequent floc formation by the hydrous oxide binder material. The particles greater than 1μ serve as suitable structural units for building up dense rapidly settling flocs, in the same manner in which larger aggregates are graded with smaller aggregates in the making of dense concrete. The practice of adding powdered limestone as a coagulant aid in reactor-type flocculation units is an application of this principle.

If, in any given water, there is a shortage of either the finer or coarser particles, the addition of the missing material will result in more efficient flocculation and clarification. If the turbidity of a given water contains a

proper distribution with respect to both types of particles, the addition of either will increase the coagulant demand without improvement in clarification. Particles that are too large to be taken up by the flocs exert no effect on coagulant demand nor on flocculation behavior.

Summary and Conclusions

Inorganic turbidity in natural waters consists principally of clay particles derived from the soil. Those particles may range up to 5μ in diameter, but it is the less than 1μ colloidal fraction that is most stable and of controlling importance in rapid flocculation. Such colloids are characterized by, and derive their stability from, an electrical double layer surrounding each particle, comprising fixed inner negative charges balanced by various adsorbed cations (Na^+, K^+, Ca^{++}, Mg^{++}, or H^+) that diffuse into the surrounding water medium. Other cations present in the dispersion medium may enter into ion exchange reactions with the initially adsorbed cations, in accordance with the law of mass action and with the relative exchange adsorbabilities of the various cations. The addition of polyvalent cations to the system will repress the double layer and thus lower the stability of the particles, until a point is reached at which the particles begin to coalesce very slowly to form aggregates. Such aggregates will settle out over a long period of time, but the clarification effected by short-period settling comparable to plant practice will be negligible. Destabilization to a greater degree will increase the rate of coalescence, until finally a visible reduction in turbidity will be possible with short settling periods. The rate of coalescence at any degree of destabilization will be greater for particles having adsorbed cations that are initially Na^+ or K^+ rather than Ca^{++}, Mg^{++}, or H^+. A more important factor affecting the rate of agglomeration is the total exchange capacity of the turbidity particles, that is the total concentration of adsorbed or exchangeable cations in the system. In waters of very high exchange capacities, exceeding certain critical limits, the agglomeration following destabilization will be very rapid, resulting in large flocs and rapid clarification. Any electrolyte yielding active cations (polyvalent or H^+ cations) will produce this effect, and the presence of a hydrolyzing coagulant, such as an aluminum and iron salt, is not required. Under these conditions the rapid agglomeration of the destabilized colloidal particles also induces the agglomeration of larger noncolloidal particles that may be present. Mutual coagulation is not involved in this type of flocculation.

Most natural waters contain less than critical concentrations of exchange capacity, and for these waters the aggregates that form following destabilization are too small for rapid settling. In order to effect rapid clarification of normal waters it is necessary that a suitable agglomerating agent or binder material be present, which will bind the various small aggregates into large and rapidly settling flocs. In practice, a properly adjusted dosage of a single hydrolyzing coagulant chemical, such as an aluminum or ferric salt, will effect both actions. In alum flocculation a portion of the Al^{+++} ions are effective in destabilizing the turbidity particles, and the remainder of the ions, through hydrolysis, form insoluble hydrous oxide binder material. The dosage of alum needed for the destabilization process will equal the exchange capacity of the system, and

essentially all of the initially absorbed cations will be replaced by Al^{+++}.   The hydrous oxide required will depend upon the concentration and particle size distribution of the turbidity.

Optimum flocculation represents the attainment of a very complex equilibrium in which many variables are involved.   Thus for a given water there will be interrelated optima of conditions such as turbidity, particle size distribution, exchange capacity, pH, and alkalinity, at which proper amounts of destabilizing ions and also of hydrous oxide are produced with a minimum total coagulant dosage.   Alkalinities in excess of optimum result in waste of an equivalent amount of coagulant through production of excess binder material. At alkalinities less than optimum, not enough hydrous oxide can be produced to satisfy the binder demand of the particles.   Also, for optimum flocculation, the water must contain a suitable number of colloidal clay particles of size less than 1μ and a sufficient number of larger particles of sizes from 1μ to about 5μ. All of the exchange demand is associated with the less than 1μ fraction, but both fractions influence the binder demand.   The smaller clay particles are necessary for stabilizing the hydrous oxide particles through mutual coagulation, and also their agglomeration following destabilization will induce agglomeration of other suspended particles present.   The larger clay particles serve as building units to permit the formation of compact, dense flocs.   If the water contains more of either type of particle than is needed for optimum results, the coagulant demand will be increased without corresponding benefit. If the water is initially deficient in colloids, its flocculation behavior may be improved by the addition of bentonite or other clay colloids of high exchange capacity, activated silica, or other negatively charged colloidal material.   The addition of bentonites or other colloidal clays may also be helpful in providing buffer capacity to a water initially low in bicarbonate alkalinity.

Detergency, in a sense, is the opposite of flocculation, and the presence of detergents or surface active agents inhibits flocculation in varying degrees. They may peptize the turbidity particles, increasing their stability and thus inhibiting flocculation or preventing it altogether.   Sequestering agents, such as hexametaphosphate, may similarly peptize the turbidity particles and, in addition, may inactivate an amount of coagulant equivalent to the number of active cations sequestered.